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# On Alkyl Malonic Nitriles and their Derivatives

A DISSERTATION

SUBMITTED TO THE FACULTIES OF THE GRADUATE SCHOOLS OF ARTS, LITERATURE, AND SCIENCE, IN CANDIDACY FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

BY JOHN C. HESSLER

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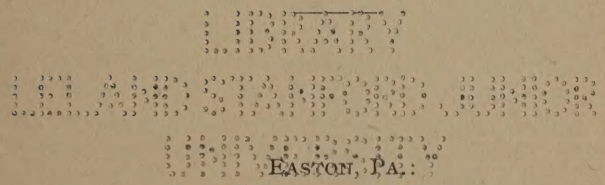

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# On Alkyl Malonic Nitriles and their Derivatives.

By John C. Hessler.

Monalkylated derivatives of malonic nitrile were prepared by P. Henry,[1] in 1889, by the distillation of the corresponding alkyl cyanacetamides with phosphorus pentoxide, but, except the determination of a few physical constants, no study of them has yet been made.

The experiments described in this paper were carried out at the suggestion and under the direction of Prof. Nef. Their object was the preparation and study of certain alkyl malonic nitriles, their salts, and other derivatives. The substances specifically studied were ethyl and benzyl malonic nitriles; the former had been prepared by Henry.[2]

The synthesis of alkyl malonic nitriles requires the preparation of alkyl cyanacetic ethers, which will now be described.

*Preparation of Crude Ethylcyanacetic Ether.*

The product obtained by Henry[3] from cyanacetic ether and ethyl iodide by the Conrad-Limpach method was found to be a mixture of about 30 per cent. diethylcyanacetic ether and 70 per cent. monethylcyanacetic ether.

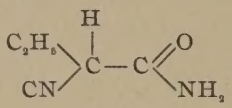
Fifty grams cyanacetic ether were mixed with 250 cc. absolute alcohol and treated with an alcoholic solution of 10.15 grams (1 atom) of sodium. 88 grams (1.25 molecules) of ethyl iodide were then added. The temperature rose to 40°, and within twenty minutes the solution was neutral to litmus. After the removal of the excess of alcohol and ethyl iodide by distillation water was added and the separated oil extracted

1 Henry: Jahresber., 1889, 637; Belg. Acad. Bull. [3], 18, 670
2 Henry: *Ibid.*
3 Henry: *Ibid.*

with ether. The dried ether solution gave, on distillation, a substance boiling at 123°–124° at 50 mm., and at 206°–211° at ordinary pressure. The yield was 46 grams, or 74 per cent. of the theoretical.

Thus prepared, crude ethylcyanacetic ether is a light and colorless oil, with an agreeable, ethereal odor. It is soluble in water to only a slight extent, but readily miscible with alcohol, benzene, and ether.

Sodium carbonate has no effect upon the substance, but aqueous sodium hydroxide dissolves it completely after several hours.

*Ethylcyanacetamide*,[1]  , was made by

treating 20 grams crude ethylcyanacetic ether with 17.2 grams (2 molecules) of 28 per cent ammonia. After twenty-four hours the amide which had crystallized out was filtered off, and the mother-liquor distilled at reduced pressure (24 mm.). The water, which distilled at 30°–35°, carried with it a small amount of a light oil; a considerable amount of the oil followed at 110°–112°, and, finally, a product boiling at 180°–190°, which solidified in the condenser. This was ethylcyanacetamide (weight 4.5 grams). The total yield of amide from 20 grams oil was 8.5 grams.

The substance boiling at 110°–112° was separated from the water in the usual manner, and found to be pure diethylcyanacetic ether (see below). Its weight was 4.5 grams.

Ethylcyanacetamide is an odorless solid, soluble in water and in alcohol, almost insoluble in ligroin and in ether, and crystallizing from alcohol in colorless right prisms, which melt at 113°. The substance distils at reduced pressure (180°–190° at 24 mm.) without decomposition, and sublimes at temperatures near its melting-point. Toward sodium carbonate it is indifferent, but it is readily dissolved by aqueous sodium hydroxide, with evolution of ammonia. A portion was re-

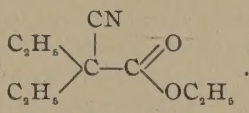
[1] Cf. Henry: *Ibid.*

crystallized twice from alcohol, and dried in an air-bath at 80° and *in vacuo* over sulphuric acid.

A nitrogen determination gave the following result:

0.0804 gram gave 19 cc. $N_2$ at 25° C. and 742 mm.

| | Calculated for $C_5H_8NO$. | Found. |
|---|---|---|
| N | 25.00 | 25.04 |

*Diethylcyanacetic Ether*,[1]  .—As stated above, crude ethyl cyanacetic ether made by the Conrad-Limpach method (Henry) was found to contain a considerable amount of a substance apparently unaffected by standing twenty-four hours with a concentrated solution of ammonia. The behavior of the crude oil toward sodium hydroxide, which dissolves the greater portion in a few minutes, and the remainder only after several hours, also establishes the presence of a neutral product. Its amount is found by treating 5 grams of the crude oil in ethereal solution with caustic soda. 1.5 grams remain unaffected by the alkali. This neutral product, which was obtained in large quantity in the conversion of crude ethylcyanacetic ether into the amide (see above), now boils at 215°–216°. It was redistilled and an analysis made, the resulting figures agreeing with those required by diethylcyanacetic ether.

I. 0.1434 gram substance gave 0.3317 gram $CO_2$, and 0.1159 gram $H_2O$.

II. 0.2139 gram substance gave 16.2 cc. $N_2$ at 25° and 745.6 mm.

| | Calculated for $C_9H_{15}NO_2$. | Found. I. | II. |
|---|---|---|---|
| C | 63.90 | 63.10 | .... |
| H | 8.87 | 8.98 | .... |
| N | 8.28 | .... | 8.33 |

The substance is a colorless liquid, of pleasant odor, boiling at 215°–216°, and readily miscible with organic solvents, but insoluble in water. It is indifferent to sodium carbonate, but

[1] Cf. Hesse: Am. Chem. J., 18, 746.

slowly soluble in caustic soda. After some months' standing, even in the dark, it becomes yellow.

Diethylcyanacetic ether was treated with 28 per cent ammonia and allowed to stand two weeks. The product was recrystallized from alcohol and found to melt at 122°. Hesse[1] gives the melting-point of diethylcyanacetamide as 120° Diethylcyanacetic ether was heated with concentrated hydrochloric acid in a sealed tube to 100° C. The contents of the tube were diluted with water and extracted with ether. The acid product was removed by shaking with sodium carbonate, acidifying with dilute sulphuric acid, and extracting with ether. Distillation of the latter left an oil, of acid odor, which solidified *in vacuo* over sulphuric acid. This substance melted at 54°–56°, and remelted at 56°. Hesse[2] gives the melting-point of diethylcyanacetic acid as 57°.

Persistent efforts were made to determine whether any cyanacetic ether was present in crude ethylcyanacetic ether, but not a trace of this substance could be found.

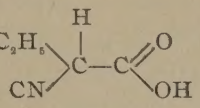
Henry[3] states that by several distillations of crude ethylcyanacetic ether he obtained a substance pure enough to be converted into amide, and that the vapor density and nitrogen determinations which he made gave figures that agreed with the theoretical. It is very unlikely, however, that he succeeded in effecting a complete separation, by fractional distillation, of diethylcyanacetic ether, boiling at 215°–216°, and ethylcyanacetic ether, boiling less than 10° lower. He states, further, that the ethylcyanacetic ether made by him was identical with that obtained by Haller[4] and by L. Henry[5] by the same method, and by Markownikow[6] from mercury and potassium cyanides and *a*-brombutyric ether.

The mixed character of the product obtained by the action of cyanacetic ether and sodium alcoholate with ethyl iodide makes it probable that similar reactions carried out with other iodides always give mixtures of mono- and dialkylated cyan-

[1] Cf. Hesse : Am. Chem. J., **18**, 746.
[2] Hesse : *Ibid.*
[3] Henry : Belg. Acad. Bull. [3], **18**, 670.
[4] Haller : Compt. rend., **104**, 1627.
[5] L. Henry : *Ibid.*, **104**, 1619.
[6] Markownikow : Ann. Chem. (Liebig), **182**, 330.

acetic ethers. For the same reason it seems unlikely that monalkylated malonic ethers have ever been obtained pure. The boiling-points of the substances are so close together that separation by fractional distillation is impossible, while the very slight differences in their composition prevent the detection in the monalkylated substances of small amounts of the dialkylated bodies.

Many similar cases have been observed and described, one of them by Nef[1] in his paper on acetoacetic ether derivatives.

*Ethylcyanacetic Acid*,  , was prepared by

treating 18 grams of crude ethylcyanacetic ether in ethereal solution with aqueous sodium hydroxide, which leaves diethylcyanacetic ether intact. The alkaline solution was treated with an excess of dilute sulphuric acid and extracted with ether. Distillation of the ether left a slightly colored oil of acid odor, distilling undecomposed at reduced pressure (160°-161° at 24 mm.). The yield was 6 grams.

A nitrogen determination gave the following result:

0.1152 gram substance 13 cc. $N_2$ at 26° C. and 747.3 mm.

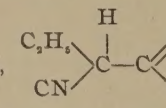
| | Calculated for $C_5H_7NO_2$. | Found. |
|---|---|---|
| N | 12.39 | 12.39 |

Ethylcyanacetic acid is a colorless, hygroscopic liquid with a faint odor, soluble in alcohol and in ether, and very soluble in water. At reduced pressure it distils without decomposition, but it is decomposed at ordinary pressures into carbon dioxide and butyronitrile, as is shown by the following experiment:

Three and four-tenths grams of the acid were heated in a flask to 170° C., at which temperature the substance decomposed into carbon dioxide and an oil boiling at 120°–140°. Weight of oil, 2 grams. Redistilled, the oil boiled at 118°–120°, and had the characteristic odor and other properties of butyronitrile.

[1] Nef: Ann. Chem. (Liebig), **266**, 116–122.

A brown liquid remained in the flask and solidified on cooling. This was soluble in sodium carbonate and precipitated by dilute sulphuric acid. Recrystallized from alcohol, the substance melted at 107°.5. It was undoubtedly slightly impure ethylmalonic acid (melting at 111°.5 when pure) formed by the saponification of some of the ethylcyanacetic acid.

*Silver Salt of Ethylcyanacetic Acid*,  .—

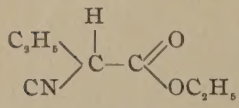
This substance was made by neutralizing ethylcyanacetic acid with ammonia and adding concentrated silver nitrate. The precipitated silver salt was washed with cold water and dried *in vacuo*. A silver determination, made by ignition of the substance, gave the following result:

0.1990 gram substance gave 0.0970 gram silver.

| | Calculated for $C_5H_6NO_2Ag$. | Found. |
|---|---|---|
| Ag | 49.09 | 48.74 |

The silver salt is crystalline and, at first, perfectly white, but colors slowly in the light. The vapor that escapes when the substance is heated has the odor of butyronitrile.

*Preparation of Pure Ethylcyanacetic Ether.*

 .—36 grams (about 3 molecules) of ethyl iodide were treated in a flask provided with a reversed condenser with 16.5 grams of the silver salt of ethylcyanacetic acid. Interaction took place on heating to 50°–55°, and 9.5 grams, *i. e.* 90 per cent of the theory, of ethylcyanacetic ether, boiling at 207°–209°, were obtained. To insure the removal of all ethyl iodide the product was heated with about 1 gram of silver ethylcyanacetate, and then redistilled.

An analysis gave the following results:

0.2018 gram substance gave 0.4430 gram $CO_2$, and 0.1428 gram $H_2O$.

| | Calculated for $C_7H_{11}NO_2$. | Found. |
|---|---|---|
| C | 59.57 | 59.86 |
| H | 7.80 | 7.86 |

Pure ethylcyanacetic ether is a colorless oil having a faint, sweet odor, noticeably different from that of the crude substance obtained by the Conrad-Limpach method. Its specific gravity at 22°.3 is 0.985.

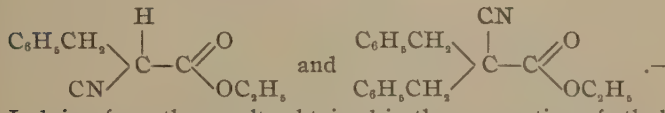
*Action of Dry Sodium Cyanacetic Ether with Ethyl Iodide.*

It seemed possible that the formation of the relatively large amount of diethylcyanacetic ether obtained in the Conrad-Limpach reaction was due to the presence of alcohol, and that, if dry sodium cyanacetic ether were treated with ethyl iodide, the amount of dialkylated substance might be considerably diminished. This proved to be the fact.

Dry sodium cyanacetic ether was prepared by adding sodium wire to a solution of cyanacetic ether in absolute ether. The yield of dry salt was regularly 95 per cent of the theory. 15 grams of sodium cyanacetic ether were heated in a sealed tube to 100° with 17.3 grams (1 molecule) of ethyl iodide and 10 cc. absolute ether. The contents of the tube were treated with water, and extracted with ether. Distillation of the ether left an oil boiling at 207°–209°, which had all the properties of crude ethylcyanacetic ether. Yield, 12 grams. Treatment with caustic soda showed that the product contained 1.5 grams, *i. e.* 12.5 per cent, of diethylcyanacetic ether. This method does not, therefore, avoid the formation of the dialkylated body, although it reduces its amount.

*Action of Cyanacetic Ether with Alcoholic Sodium Ethylate and Benzyl Chloride.*

*Mono- and Dibenzylcyanacetic Ethers,*




Judging from the results obtained in the preparation of ethylcyanacetic ether by the Conrad-Limpach method it seemed very likely that an attempt to prepare benzylcyanacetic ether

by the same method would likewise give a mixture of products.

Cassirer,[1] who was the first to carry out this experiment, states that he obtained from equimolecular quantities of cyanacetic ether, benzyl chloride, and sodium ethylate a heavy oil, which was saponified by alcoholic caustic potash to dibenzylcyanacetic acid. He seems to have overlooked entirely the small amount of monobenzylcyanacetic ether formed.

The experiment was carried out as follows: 20 grams cyanacetic ether, dissolved in absolute alcohol, were treated with an alcoholic solution of 4.07 grams (1 atom) of sodium, and with 22.4 grams (1 molecule) of benzyl chloride. The mixture was warmed on a water-bath for fifteen minutes, and found to be neutral to litmus. The alcohol having been distilled off, the residue was treated with water, extracted with ether, and the ethereal solution dried with calcium chloride. Distillation of the ether left a dark oil, which was distilled at reduced pressure (21 mm.), the fractions obtained boiling as follows: 1. below 78°; 2. 78°–228°; 3. 178°–238°. The first fraction consisted of alcohol and benzyl chloride, the second of benzyl chloride and a very small amount of cyanacetic ether, and the third of a colorless liquid boiling at 176°–183° at 21 mm., and a viscous, yellow liquid boiling at 234°–236° at the same pressure. These two substances were mono- and dibenzylcyanacetic ethers, respectively (see below). The yield of the former was only 2–3 grams, that of the latter 10-12 grams.

Owing to the fact that so small an amount of monobenzylcyanacetic ether was formed by the Conrad-Limpach method, it seemed better to treat dry sodium cyanacetic ether with benzyl chloride.

*Action of Dry Sodium Cyanacetic Ether with Benzyl Chloride.*

Twenty-seven grams of sodium cyanacetic ether were mixed in a flask with 25 grams (1 molecule) of benzyl chloride and heated gently. Reaction began at 65°, and was complete at 80°. The product was treated with water, and the separated oil extracted with ether. The residue remain-

[1] Cassirer: Ber. d. chem. Ges., **25**, 3028.

ing after the evaporation of the ether was distilled at reduced pressure (20 mm.) in fractions boiling as follows:

| Fraction. | Temperature. | Weight. Grams. |
|---|---|---|
| 1 | 65°–76° | 7.8 |
| 2 | 76°–120° | 4.2 |
| 3 | 165°–210° | 11.3 |
| 4 | 210°–233° | 6.0 |

The first fraction consisted of benzyl chloride. The second was separated, by treatment with aqueous alkali, into benzyl chloride and an oil which crystallized on standing over sulphuric acid, melted at 66°–67°, and had the other properties of cyanacetic acid. Cyanacetic ether was, therefore, present in the second fraction.

The third portion was redistilled at reduced pressure (20 mm.) and found to boil chiefly at 176°–183°. It had all the properties of the corresponding fraction obtained by the Conrad-Limpach method. The oil boiling at 176°–183° was again distilled at 20 mm., and the portion boiling at 176° was analyzed, with the following results:

I. 0.1758 gram substance gave 0.4557 gram $CO_2$, and 0.1044 gram $H_2O$.

II. 0.2075 gram substances gave 13.1 cc. $N_2$ at 22° and 1.457 mm.

| | Calculated for. $C_{13}H_{13}NO_2$. | Found. I. | II. |
|---|---|---|---|
| C | 70.93 | 70.69 | .... |
| H | 6.40 | 6.59 | .... |
| N | 6.90 | .... | 7.03 |

Three preparations, aggregating 42 grams of sodium cyanacetic ether, gave 16.4 grams of oil boiling at 165°–210° at 21 mm., from which 13.3 grams of almost pure benzylcyanacetic ether, boiling at 176°–185° at 21 mm., were obtained. Benzylcyanacetic ether is a colorless, limpid oil, having a faint aromatic odor. It is insoluble in water, but readily miscible with organic solvents. Toward sodium carbonate the substance is indifferent, but it reacts instantly with caustic soda, forming the sodium salt of benzylcyanacetic acid. If the alkaline solution is heated, ammonia is given off and the sodium salt of benzylmalonic acid is formed. With 28 per

cent ammonia, benzylcyanacetic ether reacts at once, forming benzylcyanacetamide.

The highest boiling fraction (4) obtained by heating dry sodium cyanacetic ether with benzyl chloride (see above) was redistilled at reduced pressure (20 mm.), and the portion boiling above 230° was treated in ethereal solution with aqueous sodium hydroxide, to remove any benzylcyanacetic ether which might be present. Distillation of the ether left a yellow oil boiling at 237° at 25 mm. Several attempts to solidify it proving unsuccessful, the substance was analyzed as a thick syrup, which had all the properties of the corresponding product obtained by the Conrad-Limpach method.

The analysis gave the following figures:

I. 0.4015 gram substance gave 1.1349 grams $CO_2$, and 0.2334 gram $H_2O$.

II. 0.1270 gram substance gave 0.3606 gram $CO_2$, and 0.0741 gram $H_2O$.

III. 0.5680 gram substance gave 24.6 cc. $N_2$ at 22° C. and 747 mm.

| | Calculated for $C_{19}H_{19}NO_2$. | Found. I. | II. | III. |
|---|---|---|---|---|
| C | 77.81 | 77.09 | 77.44 | .... |
| H | 6.48 | 6.46 | 6.48 | .... |
| N | 4.78 | .... | .... | 4.83 |

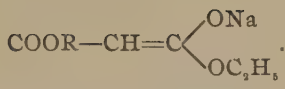
Dibenzylcyanacetic ether, obtained and analyzed as just described, in the form of a thick, viscous, yellow syrup, solidified after several weeks, forming large, colorless crystals, melting at 33°. The substance is insoluble in water and indifferent toward aqueous alkalies, but dissolves readily in alcohol and in ether.

*Constitution of Sodium Cyanacetic Ether.*

The work of Nef on acetoacetic ether, malonic ether, the nitroparaffins, etc., proves that the metallic salts formed by these compounds have the metal bound to oxygen. By analogy, sodium cyanacetic ether must have the constitution,

$$CN—CH=C\begin{matrix}ONa \\ OC_2H_5\end{matrix}, \qquad (I)$$

like that of sodium malonic ether,



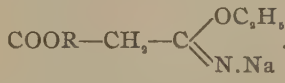
In connection with his experiments on cyanogen and isocyanogen compounds, Nef[1] was led to the consideration of another possible formula for the salt, namely,

$$COOC_2H_5—CH=C=N.Na. \qquad (II)$$

A salt of this constitution could indeed be formed by addition of sodium ethylate to the cyanogen group of the free cyanacetic ether,

$$COOR—CH_2—C\vdots N,$$

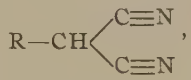
and subsequent loss of alcohol from the resulting addition-product,



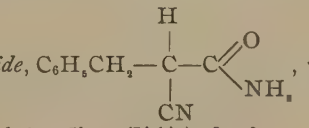
The formation of salts in the case of malonic nitrile,

$$CN—CH_2—C\equiv N,$$

and its monalkylated substitution-products,



does, in all probability, take place in this manner. The facts known at present, however, in regard to cyanacetic ether, point conclusively to formula (I) as representing the constitution of its sodium salt. Caustic alkalies and dilute acids convert the substance into cyanacetic acid, and ammonia forms with it cyanacetamide, in each of which substances the cyanogen group is unquestionably intact. This shows that the carbethoxy and not the cyanogen group is the point of attack when cyanacetic ether is treated with reagents. The same statement holds good in the case of its monalkylated substitution-products.

*Benzylcyanacetamide*,  , was prepared

[1] Nef : Ann. Chem. (Liebig), **287**, 281.

from pure benzylcyanacetic ether by treatment with a 28 per cent solution of ammonia. After twenty-four hours the crystalline mass was filtered off, washed with water, and recrystallized from alcohol.

An analysis resulted as follows:

I. 0.1980 gram substance gave 0.4990 gram $CO_2$, and 0.1036 gram $H_2O$.

II. 0.1007 gram substance gave 14.6 cc. $N_2$ at 22° C. and 744.2 mm.

| | Calculated for $C_{10}H_{10}N_2O$. | Found. I. | II. |
|---|---|---|---|
| C | 68.96 | 68.74 | .... |
| H | 5.74 | 5.81 | .... |
| N | 16.09 | .... | 16.16 |

For the preparation of benzylcyanacetamide in quantity it is much more economical to treat crude benzylcyanacetic ether, boiling at 165°–210° at 20 mm., directly with ammonia, and to free the product from a small amount of adhering dibenzylcyanacetic ether by recrystallization from alcohol. In this way it is possible to obtain about 15 grams of the amide from 50 grams of sodium cyanacetic ether.

Benzylcyanacetamide crystallizes from alcohol in large, colorless, right prisms melting at 130°, and from water in white needles. In ligroin and in ether it is only slightly soluble. Toward sodium carbonate the substance is indifferent, but sodium hydroxide dissolves it readily, even at the ordinary temperature, evolving ammonia, and forming the sodium salt of benzylcyanacetic acid (see below). At reduced pressure benzylcyanacetamide distils with little or no decomposition.

*Action of Phosphorus Pentachloride upon Benzylcyanacetamide.*

*Benzylmalonic Nitrile*, $C_6H_5CH_2CH(CN)_2$.—4.4 grams benzylcyanacetamide and 2.1 grams phosphorus pentachloride were mixed in a flask having a receiver, and the flask was exhausted to 20 mm., and heated. At 74° the mixture began to melt and to give off hydrochloric acid gas. The temperature was raised gradually until there was quiet fusion and the contents of the flask distilled over into the receiver. The yield of distillate, which solidified at once, was 3.2 grams, or 84 per

cent of the theory. The proportions of benzylcyanacetamide and of phosphorus pentachloride taken, correspond to 5 molecules of the former and 2 of the latter, similar proportions of cyanacetamide and of the pentachloride having been found by Hesse[1] to give the best yield of malonic nitrile. The substance was recrystallized from alcohol and dried over sulphuric acid.

An analysis gave the following results:

I. 0.1356 gram substance gave 0.3828 gram $CO_2$, and 0.0641 gram $H_2O$.

II. 0.1084 gram substance gave 17.5 cc. $N_2$ at 20°.5 C. and 739.1 mm.

| | Calculated for $C_{10}H_8N_2$. | Found. I. | II. |
|---|---|---|---|
| C | 76.92 | 76.99 | .... |
| H | 5.13 | 5.25 | .... |
| N | 17.95 | .... | 17.99 |

Benzylmalonic nitrile is soluble in alcohol, ether, benzene, and acetic ether; sparingly soluble in ligroin (70°–80°) and in water. From alcohol it crystallizes in large, white rhombohedra melting at 91°; from ligroin and from water in long needles. The substance distils undecomposed at reduced pressure (174° C. at 23 mm.). Caustic soda dissolves the dry solid and extracts it from its ethereal solution. If the alkaline solution is poured at once into dilute acids, benzylmalonic nitrile is regenerated; if allowed to stand twenty-four hours at the ordinary temperature, ammonia is evolved, and the sodium salt of benzylcyanacetic acid is formed; if heated, more ammonia is given off, and the solution then contains the sodium salt of benzylmalonic acid.

*Sodium Salt of Benzylmalonic Nitrile*, $C_6H_5CH_2\underset{\displaystyle CN}{\underset{|}{C}}=C=N.Na$.

—This substance was prepared by treating 4 grams of benzylmalonic nitrile in absolute benzene solution with 0.6 gram (a slight excess) of sodium. Only slight action taking place at the ordinary temperature, the mixture was warmed and allowed to stand over night. The precipitated sodium salt was

[1] Hesse: Am. Chem. J., 18, 726.

washed with benzene, and dried *in vacuo* over sulphuric acid. The yield was 3.5 grams, or 78 per cent of the theory.

A sodium determination resulted as follows:

0.2106 gram substance gave 0.0860 gram $Na_2SO_4$.

| | Calculated for $C_{10}H_7N_2Na$. | Found. |
|---|---|---|
| Na | 12.92 | 13.22 |

The salt is an almost white, amorphous powder, which absorbs moisture from the air, and then becomes dark and undergoes decomposition. Poured into dilute acids, the substance regenerates benzylmalonic nitrile in the form of a white, bulky precipitate. The salt was dissociated into benzylmalonic nitrile and sodium hydroxide on addition of water; on standing twenty-four hours most of the precipitated benzylmalonic nitrile redissolved, but a small amount remained undissolved after three days. This was accordingly filtered off, dried, and found to melt at 130°. When it was mixed with pure benzylcyanacetamide the melting-point of the latter was not lowered. The substance was, therefore, taken to be benzylcyanacetamide, formed by the addition of water to benzylmalonic nitrile. The filtrate contained the sodium salt of benzylcyanacetic acid, as was proved by acidifying with dilute sulphuric acid and extracting with ether. Evaporation of the ether left a substance melting at 101°–102° when purified, and identical in every respect with benzylcyanacetic acid (see below).

*Behavior of Sodium Benzylmalonic Nitrile when Heated.*—4 grams of the sodium salt were heated in a flask, and began to decompose at 120° C. At higher temperatures the substance swelled up to a black mass several times its original bulk. The flask was accordingly exhausted to 20 mm. and carefully heated. As a result 0.7 gram of an oil, boiling at 120°–140° at the reduced pressure, was obtained. Hot water extracted from the black residue a substance which was precipitated as a slimy, brown solid on the addition of dilute nitric acid. This proved to be the so-called azulmic acid. A strong odor of prussic acid was noticed in the filtrate from the azulmic acid. Silver nitrate was therefore added, and a precipitate of silver cyanide ob-

tained. Its amount corresponded to 0.4–0.5 gram of sodium cyanide, or 36–45 per cent of the theory.

The oil boiling at 120°–140° was redistilled and analyzed with the following results:

I. 0.1222 gram substance gave 0.3724 gram $CO_2$, and 0.0763 gram $H_2O$.

II. 0.1401 gram substance gave 13.65 cc. $N_2$ at 16° C. and 743.5 mm.

| | Calculated for $C_9H_9N$. | Found. I. | II. |
|---|---|---|---|
| C | 82.44 | 83.06 | .... |
| H | 6.87 | 6.94 | .... |
| N | 10.69 | .... | 11.14 |

The figures obtained agree fairly well with those calculated for hydrocinnamic nitrile.[1] That the oil was actually this substance was proved by its conversion into hydrocinnamic acid when heated in a sealed tube with concentrated hydrochloric acid.

*Silver Salt of Benzylmalonic Nitrile*, $C_6H_5CH_2—C(CN)=C=N.Ag$.—This substance was made by the method of Comstock and Kleeberg[2] and Tafel and Enoch.[3]

To a cold solution of 1.56 grams benzylmalonic nitrile in 150 cc. 66 per cent alcohol were added 1.7 grams (1 molecule) of silver nitrate in concentrated aqueous solution, and then, drop by drop, the calculated amount of half-normal caustic potash. A bulky, amorphous, white precipitate was formed, which was thoroughly washed by decantation with water, and dried *in vacuo* over sulphuric acid. The yield was 2.4 grams, or 90 per cent of theory.

A silver determination gave the following result:

0.1724 gram substance gave 0.0710 gram Ag.

| | Calculated for $C_{10}H_7N_2Ag$. | Found. |
|---|---|---|
| Ag | 41.06 | 41.18 |

The silver salt can be kept indefinitely *in vacuo* over sulphuric acid, but in the air, even when protected from the

[1] Cf. Hoffman: Ber. d. chem. Ges., **7**, 520.
[2] Comstock and Kleeberg: Am. Chem. J., **12**, 498.
[3] Tafel and Enoch: Ber. d. chem. Ges., **23**, 104.

light it soon becomes black, and emits an odor like that of hydrocinnamic nitrile. When the salt is treated with dilute nitric acid, benzylmalonic nitrile is regenerated. Methyl and ethyl iodides react instantly with the substance. Heated, it begins to decompose at 80°, and at higher temperatures becomes a hard, black mass. Ether then extracts some tarry material, and leaves a gray substance having the properties of silver cyanide. The dissociation of the silver salt of benzylmalonic nitrile into silver cyanide, and that of the sodium salt into sodium cyanide, makes it very probable that their constitution is to be represented by the formula

$$C_6H_5CH_2C(CN)=O=N.M.$$

Assuming with Nef[1] that the double cyanides and fulminates and the double salts of isonitriles with cyanide of silver[2] have the constitution:

AgNC : CNK ;
AgONC : CNOK ;
RNC : CNAg,

it will be seen that the monalkylated malonic nitrile salts have an analogous constitution. Since Gautier has proved that potassium cyanide sets free the isonitrile from its double salt,

RNC : CNAg,

it was hoped that the silver salt of benzylmalonic nitrile might dissociate in an analogous manner. An experiment carried out with this object in view resulted as follows:

Silver benzylmalonic nitrile (3 grams) was added to aqueous potassium cyanide. The solution obtained was filtered from a white, insoluble substance, and treated with dilute nitric acid. This produced a precipitate of silver cyanide weighing 1.2 grams, or 80 per cent of the theory. The substance insoluble in the solution of potassium cyanide melted

[1] Ann. Chem. (Liebig), **298**, 313. This question is being investigated experimentally in this laboratory and will include a study of the ferro- and the ferricyanides. J. U. Nef.

[2] Gautier : Ann. chim. phys. [4,] **17**, 203.

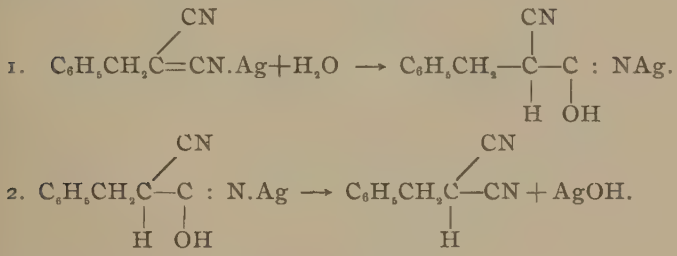
at 90° when recrystallized from ligroin, and had the other properties of benzylmalonic nitrile. Its weight was 1.1 grams, or 68 per cent of the theory. That this substance was actually benzylmalonic nitrile was proved by two nitrogen determinations, which gave the following results:

I. 0.1601 gram substance gave 25.4 cc. $N_2$ at 19°.5 C. and 738.5 mm.

II. 0.0984 gram substance gave 16 cc. $N_2$ at 23°.5 C. and 738.1 mm.

| | Calculated for $C_{10}H_8N_2$. | Found. I. | Found. II. |
|---|---|---|---|
| N | 17.95 | 17.75 | 17.84 |

The action of potassium cyanide seems therefore to be a simple hydrolysis, and is probably represented by the following equations:



1. $C_6H_5CH_2C(CN)=CN.Ag + H_2O \longrightarrow C_6H_5CH_2-C(CN)(H)-C(OH) : NAg.$



2. $C_6H_5CH_2C(CN)(H)-C(OH) : N.Ag \longrightarrow C_6H_5CH_2C(CN)(H)-CN + AgOH.$

3. $AgOH + KNC \longrightarrow AgNC + KOH.$

*Ethylmalonic nitrile*,[1] $C_2H_5-CH(CN)_2$.—5.6 grams of dry ethylcyanacetamide and 4.2 grams of phosphorus pentachloride were thoroughly mixed in a flask having a receiver. The apparatus was exhausted to 26 mm., and heat applied. The reaction took place at 80°, the mixture melted and became dark-colored, and hydrochloric acid gas came off in large quantities. The temperature was then raised very gradually to 100° or above, the end of the reaction being indicated by a violent frothing. This having ceased, the ethylmalonic nitrile formed distilled over at 90°–107°. The yield was 4 grams, or 85 per cent of the theory.

To free the product from any phosphorus oxychloride and ethylcyanacetamide which it might contain, it was shaken with water, dried, and redistilled.

[1] Cf. Henry: Jahresber., 1889, 637.

An analysis gave the following figures :

I. 0.1628 gram substance gave 0.3772 gram $CO_2$, and 0.0976 gram $H_2O$.

II. 0.1171 gram substance gave 0.2721 gram $CO_2$, and 0.0684 gram $H_2O$.

III. 0.1511 gram substance gave 39.2 cc. $N_2$ at 16° C. and 747.6 mm.

| | Calculated for $C_5H_6N_2$. | Found. I. | II. | III. |
|---|---|---|---|---|
| C | 63.83 | 63.20 | 63.38 | .... |
| H | 6.38 | 6.65 | 6.49 | .... |
| N | 29.79 | .... | .... | 29.85 |

Ethylmalonic nitrile is a light, colorless oil, only slightly soluble in water, but readily soluble in ether and in alcohol. Its odor is faint, and resembles that of acetamide. The substance boils at 90°–91° at 20 mm., and at 200° at the ordinary pressure (746 mm.). After a few weeks, even when kept in the dark, the oil becomes brown. It is indifferent to sodium carbonate, but dissolves readily in sodium hydroxide at the ordinary temperature with evolution of ammonia and formation of the sodium salt of ethylcyanacetic acid. If the alkaline solution is heated, more ammonia is evolved, and the sodium salt of ethylmalonic acid is formed.

*Sodium Salt of Ethylmalonic Nitrile*, $C_2H_5—\underset{\displaystyle CN}{\underset{|}{C}}=C=N.Na.$—

An ethereal solution of ethyl malonic nitrile does not react appreciably with metallic sodium even after two or three hours. If a drop of absolute alcohol is added, vigorous action begins, and an oil separates out which is insoluble in ether. A solution of ethylmalonic nitrile in pure benzene likewise reacts only very slightly with metallic sodium, even at the boiling-point of benzene. When the mixture was allowed to stand several days, however, a small amount of a slightly colored, amorphous powder was obtained. This was dried *in vacuo* over sulphuric acid, but decomposed so readily on exposure to the air that no further study of it was attempted.

*Silver Salt of Ethylmalonic Nitrile*,[1] $\begin{matrix} C_2H_5 \\ \\ CN \end{matrix}\!\!\rangle C=C=N.Ag.$—

[1] Cf. Henry : *Ibid.*

This substance was prepared in the same way as the silver salt of benzylmalonic nitrile, but greater precautions were taken to keep the temperature low.

Five grams ethylmalonic nitrile, dissolved in 50 per cent alcohol, were treated with an aqueous solution of 9 grams (1 molecule) of silver nitrate, and then with the calculated amount of a half-normal solution of caustic potash. During the addition of the alkali the mixture was kept cold by the introduction of pieces of ice, and was shaken vigorously. The amorphous, white precipitate of silver salt was washed by decantation with cold water, collected upon a filter, dried from five to ten minutes upon a clay plate, and then over concentrated sulphuric acid. Although the operations just described were carried out in a room at 2° C., the substance invariably decomposed after fifteen to twenty minutes. The decomposition was accompanied by a marked evolution of heat, and the bulky, white salt became black, pasty, and of small volume; at the same time water and an oil separated from the mass. The water held in solution a substance having an acid reaction and an odor like that of acetic or propionic acid. Ether and benzene extracted from the decomposed silver salt a small amount of a yellow oil, which was almost insoluble in water, bnt soluble in sodium carbonate and in sodium hydroxide. When these solutions were acidified the substance was apparently regenerated, but it could not be distilled without decomposition. Some of the oil was left standing several days, and deposited a white, crystalline solid melting at 134°. The amount of this substance was, however, so small that it was not examined further.

The black mass which had been treated with ether and with benzene was washed with hot alcohol and with water, and, finally, to free it from metallic silver, with dilute nitric acid. The residue thus obtained was a light gray, amorphous solid having the properties of silver cyanide. Heated, it was decomposed into silver and cyanogen, as is shown by the following results, which were obtained from independent preparations of silver ethylmalonic nitrile:

I. 0.3548 gram substance gave 0.2758 gram Ag.

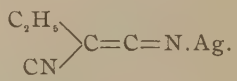
II. 0.0845 gram substance gave 0.0658 gram Ag.

III. 0.0989 gram substance gave 0.0775 gram Ag.

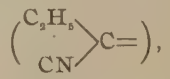
| | Calculated for AgNC. | Found. I. | II. | III. |
|---|---|---|---|---|
| Ag | 80.59 | 77.73 | 77.87 | 78.36 |

A small amount of tarry material, which adhered to the silver cyanide and escaped only upon ignition, was, no doubt, the cause of the low results.

In the case of the silver salt of ethylmalonic nitrile, as in that of the silver salt of benzylmalonic nitrile, all attempts to get both organic residues failed. Yet the spontaneous dissociation of these salts into silver cyanide, the formula of which has been determined by Nef[1] to be Ag—N=C, makes it extremely probable that in them the metal is bound to nitrogen. The formula of silver ethylmalonic nitrile is, therefore, written



Loss of silver cyanide must leave residue,



capable, no doubt, of oxidation and of polymerization, thus giving rise to a complex mixture of substances.

Most persistent efforts were made in the instance described above to determine the nature of these products. The amount of material used was inadequate for this purpose, but the work done established unquestionably their complex character.

The only positive results obtained, therefore, show that salts of monalkylated malonic nitriles dissociate into metallic isocyanides, M—N=C. In the case of silver ethymalonic nitrile this takes place spontaneously at 0°, with silver benzylmalonic nitrile at 80°, and with the corresponding sodium salt at 120°.

*Action of Malonic Nitrile with Alcoholic Sodium Ethylate and Benzyl Chloride.*

*Dibenzylmalonic Nitrile* $(C_6H_5CH_2)_2=C=(CN)_2$.—3 grams

[1] Nef: Ann. Chem. (Liebig), **287**, 265-359.

malonic nitrile (made by the method of Hesse[1] from cyanacetamide and phosphorus pentachloride) were dissolved in absolute alcohol, and treated with an alcoholic solution of 1.05 grams (1 atom) of sodium, and with 5.75 grams (1 molecule) of benzyl chloride. The temperature of the mixture rose to 40°, and common salt was precipitated. On cooling, long, white crystals of dibenzylmalonic nitrile (see below) were deposited. These were filtered off and washed with water to free them from sodium chloride. The alcoholic filtrate left, on distillation, a white, crystalline mass. This was treated with hot water, in which dibenzylmalonic nitrile is insoluble, and a small amount of monobenzylmalonic nitrile obtained. The total yield of product was 3.6 grams, fully 90 per cent of this amount being dibenzylmalonic nitrile.

An analysis of this substance gave the following results :

I. 0.1372 gram substance gave 0.4128 gram $CO_2$, and 0.0716 gram $H_2O$.

II. 0.1558 gram substance gave 16.4 cc. $N_2$ at 24° and 741.8 mm.

| | Calculated for $C_{17}H_{14}N_2$. | Found. I. | II. |
|---|---|---|---|
| C | 82.93 | 82.07 | .... |
| H | 5.69 | 5.79 | .... |
| N | 11.38 | .... | 11.58 |

Dibenzylmalonic nitrile is a white, crystalline solid melting at 131°. It dissolves in hot alcohol and in ether, is slightly soluble in hot ligroin, and insoluble in water. Toward aqueous alkalies, even when hot, it is entirely indifferent.

*Action of Dry Sodium Malonic Nitrile with Benzyl Chloride.*

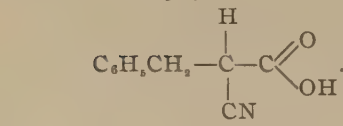
Dry sodium malonic nitrile, made according to the method of Schmidtmann,[2] was heated in a flask with the calculated amount of benzyl chloride with the expectation that a relatively larger amount of monobenzylmalonic nitrile than that produced by the Conrad-Limpach method might be formed. The reaction, accompanied by much charring, took place at 90°. The dark product was treated with boiling ligroin several times, and a white, crystalline substance obtained, which proved to be a mixture of mono- and dibenzylmalonic

[1] Hesse : This JOURNAL, **18**, 723.

[2] Schmidtmann : Ber. d. chem. Ges., **29**, 1171.

nitriles. Its amount was, however, very small. A similar result was obtained by heating dry sodium malonic nitrile with benzyl chloride and absolute ether in a sealed tube at 150°

*Benzylcyanacetic Acid* (*α-Cyan-β-phenylpropionic Acid*),



.—This substance was prepared by treating crude benzylcyanacetic ether in ethereal solution with aqueous sodium hydroxide and adding the alkaline solution to an excess of dilute sulphuric acid. The separated oil was extracted with ether, the ether dried, and distilled. The acid was thus obtained as a liquid, which solidified when cooled. It was recrystallized from benzene and an analysis made with the following results:

I. 0.1140 gram substance gave 0.2856 gram $CO_2$, and 0.0543 gram $H_2O$.

II. 0.2068 gram substance gave 15 cc. $N_2$ at 20°.5 C. and 741.6 mm.

| | Calculated for $C_{10}H_9NO_2$. | Found. I. | II. |
|---|---|---|---|
| C | 68.59 | 68.33 | .... |
| H | 5.14 | 5.29 | .... |
| N | 8.00 | .... | 8.11 |

Benzylcyanacetic acid is a white, crystalline solid, melting at 101°–102°, soluble in benzene, alcohol, and ether, and somewhat soluble in water. Hot caustic soda saponifies it, forming benzylmalonic acid. The substance cannot be distilled at ordinary pressure, since it decomposes into carbon dioxide and hydrocinnamic nitrile, as is shown by the following experiment:

Two and a half grams of the acid were heated in a flask to 170°–200°, carbon dioxide being evolved in large quantities. The residue in the flask was then dissolved in ether, the ethereal solution shaken with sodium carbonate, and dried with chloride of calcium. The ether left, on evaporation, an oil boiling at 253°; weight, 1 gram, or 53 per cent of the theory. That this substance was hydrocinnamic nitrile was

proved by heating it in a sealed tube with concentrated hydrochloric acid; hydrocinnamic acid, melting at 47°–48°, was thus formed.

*Silver Salt of Benzylcyanacetic Acid*, $C_6H_5CH_2CHCNCOOAg$. —This substance was prepared as follows: The acid was dissolved in ammonia, and the excess of the latter removed over sulphuric acid. The white ammonium salt, which had crystallized out, was redissolved in water and treated with a concentrated solution of silver nitrate. The silver salt was thus obtained as an amorphous, white precipitate, which became crystalline on standing. It was washed with water and dried over sulphuric acid. An analysis gave the following results:

I. 0.1270 gram substance gave 0.0480 gram Ag.

II. 0.0882 gram substance gave 0.0337 gram Ag.

| | Calculated for $C_{10}H_8NO_2Ag$. | Found. I. | II. |
|---|---|---|---|
| Ag | 38.29 | 37.80 | 38.21 |

The silver salt is precipitated, also, when concentrated silver nitrate is added directly to a concentrated aqueous solution of the acid. It is a heavy, white solid, which darkens slowly in the light. Heated to 140° it melts with decomposition, giving off a vapor having the odor of hydrocinnamic nitrile.

*Benzoylbenzylmalonic Nitrile*, $\begin{matrix} C_6H_5CH_2 \\ C_6H_5CO \end{matrix}\!\!>\!C=(CN)_2$. — 2.7 grams of benzoyl chloride, dissolved in 20 cc. absolute ether, were treated in the cold with 3.4 grams (1 molecule) of sodium benzylmalonic nitrile. After twenty-four hours the benzoylbenzylmalonic nitrile was obtained as a crystalline mass. The substance was separated from the sodium chloride by means of boiling ether, recrystallized once from ether, and dried *in vacuo* over sulphuric acid. Yield 3 grams, or 60 per cent of the theory. A nitrogen determination gave the following result:

0.1579 gram substance gave 15.4 cc. $N_2$ at 19°.5 C. and 743.6 mm.

| | Calculated for $C_{17}H_{12}N_2O$. | Found. |
|---|---|---|
| N | 10.77 | 10.99 |

Thus prepared, benzoylbenzylmalonic nitrile is a perfectly white, crystalline solid, melting at 100°, sparingly soluble in hot ligroin (70°–80°), and readily soluble in warm ether. It is unaffected by water and by sodium carbonate, but is decomposed by hot alcohol and by aqueous caustic soda, as is established by the following experiments:

*a*. The substance was heated for half an hour with absolute alcohol in a flask provided with a reversed condenser. Distillation of the alcohol left an oil from which a white, crystalline solid was deposited. The crystal-form and the melting-point (91°) of the solid proved it to be benzylmalonic nitrile.

The oil was readily identified as benzoic ether

*b*. An ethereal solution of benzoylbenzylmalonic nitrile was treated with caustic soda and the alkaline solution poured at once into dilute sulphuric acid. The product was a mixture of benzoic acid and benzylmalonic nitrile; these were separated by treatment with sodium carbonate, and thoroughly identified.

*Brombenzylmalonic Nitrile*, $C_6H_5.CH_2\diagdown\atop\diagup Br\!\!>C=(CN)_2$. — This substance was prepared by adding 2 grams of sodium benzylmalonic nitrile to an absolute ethereal solution of 1.8 grams (2 atoms) of bromine. After twenty-four hours water was added to dissolve the sodium bromide formed, and the ethereal solution was treated with caustic soda, to insure removal of benzylmalonic nitrile. Distillation of the ether left a slightly colored solid, which was boiled, in ligroin solution, with bone-black, and thus obtained perfectly white. A portion, recrystallized from a mixture of absolute ether and ligroin (40°–60°), gave the following results on analysis:

I. 0.1713 gram gave 18.3 cc. $N_2$ at 20°.5 and 748.2 mm.

II. 0.0760 gram contained 0.02582 gram Br.

| | Calculated for $C_{10}H_7N_2Br$. | Found. I. | Found. II. |
|---|---|---|---|
| N | 11.91 | 12.05 | .... |
| Br | 34.04 | .... | 33.97 |

The substance dissolves readily in ether, but is difficultly soluble in water. It crystallizes from alcohol in thin plates with serrated edges, and from ligroin in fine needles melting

in each case at 119°–120°. Unlike the benzoyl compound brombenzylmalonic nitrile is not affected by aqueous sodium hydroxide. Heated, it distils with decomposition, giving off hydrobromic acid. The distillate is a solid which melts at 70° when recrystallized from alcohol; this is probably a mixture of unchanged substance and benzylmalonic nitrile, whose melting-point is given by Heuck[1] as 87°. Treatment with alcoholic potash converted brombenzylmalonic nitrile, into a dark, thick oil, which refused to solidify, and was not further examined.

*Carbethoxybenzylmalonic nitrile* (*Benzylcyanacetic Ether*), $C_6H_5CH_2 \diagdown C(COOC_2H_5) \diagup C(CN)_2$.—Four grams of sodium benzylmalonic nitrile were added to an absolute ethereal solution of 2.48 grams (1 molecule) of chlorcarbonic ether. Reaction set in at once, and was controlled by cooling the mixture with water. After twenty-four hours the sodium chloride produced was filtered off, the ether evaporated *in vacuo*, and the solid residue recrystallized from a mixture of absolute ether and ligroin (40°–60°). The yield was 3 grams, or 60 per cent of the theory. A nitrogen determination of the product gave the following result:

0.1655 gram substance gave 18.6 cc. $N_2$ at 20° and 740.8 mm.

| | Calculated for $C_{13}H_{12}N_2O_2$. | Found. |
|---|---|---|
| N | 12.28 | 12.58 |

Carbethoxybenzylmalonic nitrile is soluble to a slight extent in water and in ligroin (70°–80°), more soluble in ether, and very soluble in alcohol. It crystallizes in large, colorless prisms melting at 44°–45°. Caustic soda acts upon it slowly in the cold, but more readily when hot, evolving ammonia.

*Methylbenzylmalonic Nitrile*, $C_6H_5CH_2 \diagdown C(CH_3) \diagup C(CN)_2$. — This substance was prepared from both the silver and the sodium salt of benzylmalonic nitrile.

*a*. 3.7 grams of silver benzylmalonic nitrile were added, in

[1] Heuck: Ber. d. chem. Ges., **28**, 2253.

several portions, to 6 grams (3 molecules) of methyl iodide. The salt hissed like hot iron on coming in contact with the methyl iodide, and the latter was, therefore, diluted with 10 volumes of absolute ether. After the addition of all the silver salt the mixture was warmed to the boiling-point of the ether. The silver iodide formed was then filtered off and the ethereal solution was treated with caustic soda, dried with calcium chloride, and distilled. The ethereal distillate had a faint odor of isonitrile. The residual oil solidified, on cooling, to a colored, crystalline mass, which was obtained perfectly white by treatment, in ligroin solution, with animal charcoal. The yield of crude product was 2.2 grams, or 92 per cent of the theory. The substance was dried *in vacuo* and analyzed with the following results:

I. 0.0984 gram substance gave 0.2804 gram $CO_2$ and 0.0507 gram $H_2O$.

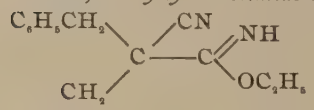
II. 0.0774 gram substance gave 11.5 cc. $N_2$ at 21°.5 C. and 747.7 mm.

| | Calculated for $C_{11}H_{10}N_2$. | Found. I. | II. |
|---|---|---|---|
| C | 77.65 | 77.70 | .... |
| H | 5.88 | 5.73 | .... |
| N | 16.47 | .... | 16.68 |

Methylbenzylmalonic nitrile is readily soluble in ether and in alcohol, and slightly soluble in water and in ligroin. It crystallizes from water in needles and from ligroin (70°–80°) in large prisms, melting at 94°–95°.

*b*. Sodium benzylmalonic nitrile reacts only very slowly with methyl iodide. After several days' standing large, colorless, hexagonal plates separated from the mixture. These melted at 94°–95°, and had all the other properties of the substance made from the silver salt.

*Action of Benzylmalonic Nitrile with Methyl Iodide and Alcoholic Sodium Ethylate.*

*Methylbenzylcyanacetimido Ethyl Ester*,  .—3 grams of benzylmalonic ni-

trile, dissolved in absolute alcohol, were treated with an alcoholic solution of 0.45 gram (1 atom) of sodium and with 2.7 grams (1 molecule) of methyl iodide. There was an evolution of heat, and the mixture became neutral in twenty minutes. The alcohol was then distilled and the residue treated with water and extracted with ether. After treatment with caustic soda the ethereal solution was dried with chloride of calcium, and the ether evaporated. An almost colorless oil remained, which distilled at reduced pressure (170° at 22 mm.) without decomposition. The yield was 3.5 grams, or 85 per cent of the theory.

An analysis gave the following results:

I. 0.1750 gram substance gave 0.4624 gram $CO_2$, and 0.1198 gram $H_2O$.

II. 0.1555 gram substance gave 18.2 cc. $N_2$ at 21° and 742.6 mm.

| | Calculated for $C_{18}H_{16}N_2O$. | Found. I. | II. |
|---|---|---|---|
| C | 72.22 | 72.07 | .... |
| H | 7.41 | 7.61 | .... |
| N | 12.96 | .... | 13.08 |

The product obtained in the case of the Conrad-Limpach reaction is, therefore, not the nitrile, but the imido ether.[1] This is a faintly aromatic, colorless oil, insoluble in water and in caustic soda. When its alcoholic solution is treated with concentrated hydrochloric acid a white precipitate of ammonium chloride is instantly formed. After standing six months the oil became so viscous that it could hardly be poured, yet all attempts to make it solidify were unsuccessful. The properties of the substance had also changed; ether dissolved it only partially, leaving a white amorphous solid. That the imido ether obtained in the reaction described above is formed from the nitrile by the addition of alcohol is proved by the behavior of methylbenzylmalonic nitrile with sodium ethylate. Methylbenzylmalonic nitrile (1.2 grams) dissolved in absolute alcohol was treated with an alcoholic solution of 0.16 gram (1 atom) of sodium. No change was noticed, except that the solution became slightly colored. After standing at

[1] Cf. Nef: Ann. Chem. (Liebig), **287**, 273, 315-8, 343. Also Hesse: Am Chem. J., **18**, 744.

the ordinary temperature over night the mixture was poured into water and the separated oil extracted with ether. A substance was obtained which boiled at 156° at 9 mm. ; weight, 1.15 grams, or 75 per cent of the theory.

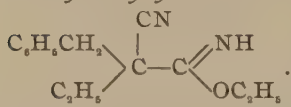
A nitrogen determination resulted as follows :

0.2066 gram substance gave 24.3 cc. $N_2$ at 21° and 746.8 mm.

| | Calculated for $C_{13}H_{16}N_2O$. | Found. |
|---|---|---|
| N | 12.96 | 13.22 |

This substance is identical in every respect with the imido ether described above.

*Ethylbenzylcyanacetimido Ethyl Ester*,



.—This compound was prepared from both ethyl and benzylmalonic nitrile.

*a*. 2 grams ethylmalonic nitrile, dissolved in absolute alcohol, were treated with an alcoholic solution of 0.5 gram (1 atom) of sodium and with 2.7 grams (1 molecule) of benzyl chloride. The temperature of the mixture rose to 50°. After the distillation of the alcohol, water was added to the residue and the separated oil extracted with ether, washed with sodium hydroxide, and dried with calcium chloride. Distillation of the ether left a product boiling at 170° at 22 mm. ; weight, 3.5 grams, or 71 per cent of the theory.

A nitrogen determination gave the following result :

0.2339 gram substance gave 25.4 cc. $N_2$ at 19° and 744.5 mm.

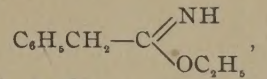
| | Calculated for $C_{14}H_{18}N_2O$. | Found. |
|---|---|---|
| N | 12.18 | 12.28 |

This substance is decomposed by concentrated hydrochloric acid, like all imido ethers, with separation of ammonium chloride. It is colorless when freshly prepared, but becomes brown on standing.

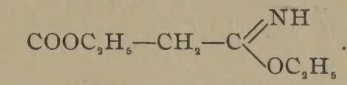
*b*. 1 gram benzylmalonic nitrile, dissolved in absolute alcohol, was treated with an alcoholic solution of 0.13 gram (1 atom) of sodium and with 2 grams (2 molecules) of ethyl

iodide. A product (0.9 gram, *i. e.*, 75 per cent of the theory) boiling at 171° at 23 mm., and identical in its properties with the imido ether described under *a* was obtained.

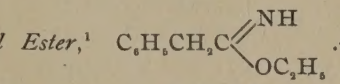
Finally, there is appended here a description of a convenient method of preparing *phenylacetimido ether*,



and *monimidomalonic ether*,



These substances are of interest especially because analogous compounds have been assumed as intermediate products in the conversion of malonic nitrile and its monalkylated derivatives into salts. A study of them will, therefore, be continued in this laboratory. Their behavior toward metals, amines, sodium ethylate, and alkyl iodides deserves special investigation.

*Phenylacetimido Ethyl Ester*,[1]  .—The hydrochloride of this substance was made from benzyl cyanide by the method of Pinner, and was obtained at first as a colorless oil, which solidified with much difficulty. The salt is perfectly white and odorless and very soluble in water, which decomposes it into phenylacetic ether and ammonium chloride.

The free imido ether was prepared from the hydrochloride by the method of Bushong :[2] 10 grams of the salt were added to an excess of 10 per cent sodium hydroxide, cooled to 7° C., and the separated oil was taken up at once with ether and dried with calcium chloride. Distillation of the ether left a colorless substance, boiling at 105°–106° at 10 mm. pressure. The yield was 6.9 grams, or 84 per cent of the theory.

A nitrogen determination gave the following result :

0.1538 gram substance gave 12 cc. $N_2$ at 23° C. and 752.6 mm.

1 Cf. Lückenbach : Ber. d. chem. Ges., **17**, 1421.

2 Am. Chem. J., **18**, 490.

| | Calculated for $C_{10}H_{13}NO$. | Found. |
|---|---|---|
| N | 8.57 | 8.75 |

The imido ether is insoluble in water and in aqueous alkalies. It distils at ordinary pressure with slight decomposition into alcohol and benzyl cyanide. Treated, in absolute ethereal solution, with metallic sodium, the imido ether gave a white, amorphous precipitate, which was not further examined.

*Monimidomalonic Ether*,[1] $CH_2\langle^{C(NH)OC_2H_5}_{COOC_2H_5}$.—The hydrochloride of this substance was made from cyanacetic ether by the method of Pinner. The salt was obtained as a colorless oil, which solidified, when shaken with cold ether, to a white, crystalline mass. It is soluble in cold water without decomposition, but on heating malonic ether is set free.

The free imido ether (made by adding the hydrochloride to cold 10 per cent sodium hydroxide) is a colorless oil, distilling at reduced pressure without decomposition. Heated at ordinary pressure, however, to 165°, it is decomposed into alcohol (75 per cent of the theoretical amount was obtained), and a thick, pasty mass, India-red in color, and insoluble in ether and in alcohol.

[1] Cf. Oppenheimer: Ber. d. chem. Ges., 28, 478.